

Differential Arrival Time of CO₂ and Associated Impurities Injected in the Subsurface



Stefan Bachu, Alberta Energy and Utilities Board
4449 – 98th Avenue NW, Edmonton, AB, T6B 2X3, Canada, E-mail: Stefan.Bachu@gov.ab.ca

D. Brant Bennion, Hycal Energy Research Laboratories Ltd.
1338A – 38th Avenue NE, Calgary, AB, T2E 6T6, Canada, E-mail Brantb@hycal.com



Abstract

Carbon dioxide sequestration in geological media is a greenhouse gas mitigation technology that is immediately available, as demonstrated by more than 45 acid gas disposal operations in western Canada. The CO₂ concentration at these injection sites varies between 14% and 98%, with the balance made of H₂S and minor amounts of hydrocarbon gases. In a few instances acid gas injected in a depleted gas reservoir broke through at neighboring producing wells, and in one case it was observed that CO₂ broke through first, followed later by H₂S. This observation led to the implementation of an experimental laboratory program for assessing the differential arrival time at an observation or producing well of CO₂ and various impurities contained in a CO₂ stream injected into a water-saturated porous medium. Experiments are being conducted with CO₂ containing 5% H₂S, CH₄, N₂, NO_x or SO_x, which are impurities characteristic of CO₂ streams captured from gas processing and power plants. Additional experiments were carried out for streams containing 2% and 30% H₂S. The in-situ conditions are characteristic of a specific acid gas injection site in northwestern Alberta.

Laboratory Setting

The Hycal lab is equipped with Class 1 explosion-proof wiring, real time multi-location constant monitoring for H₂S and combustible gas levels, remote camera monitoring and data acquisition, two high rate carbon scrubbing air cleaning systems for zero external emissions of H₂S, complete remote oxygen supply for all operators working in contact with acid gas, and a complete external monitoring and safety system. All equipment is Hastalloy and sour gas rated.



Exterior view of Hycal H₂S isolation lab.

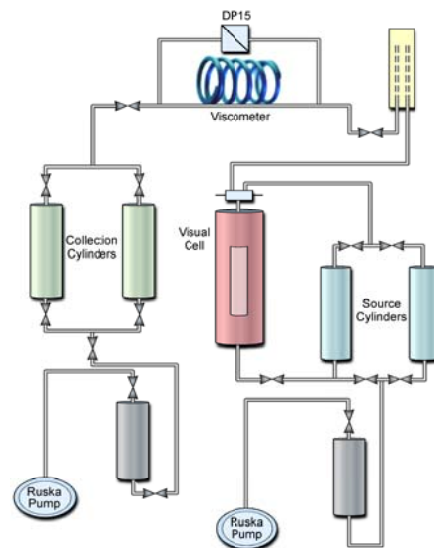


Interior view of the H₂S facility.

Laboratory Apparatus

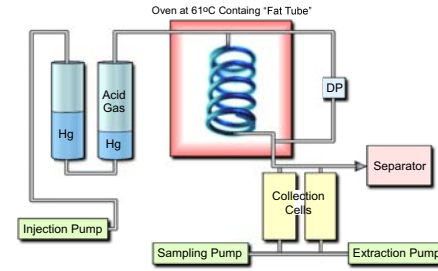
The experimental program consisted of two phases: the first to measure and test the differential solubility of CO₂ and H₂S under static reservoir conditions (no flow), and the second to measure the differential arrival time of CO₂ and impurities under flow at reservoir conditions.

The PVT (pressure-volume-temperature) apparatus for observing the phase behavior of the acid gas mixture under static conditions normally includes a visual cell, source cylinders, capillary tube, collection cylinder, cleaning solvent bomb, oven, cathetometer for accurate phase volume measurement at system temperature and pressure, buffers and pumps. A high pressure test cylinder was substituted for the normal visual cell. The high-pressure piston test cylinder has a pressure rating of 10,000 psi at over 300°F. Connected to the pressure cell are high pressure source cylinders containing the fluids of interest. Displacing fluid into the bottom of the source cylinder with the pump transfers a corresponding volume into the pressure cell. The fluids can be mixed in prescribed ratios to within about 0.02 cc. The cylinders are normally 660 cc 316 SS cylinders with a pressure rating of 10,000 psi.



Schematic representation of the apparatus used for gas solubility measurements under static (no flow) reservoir conditions of pressure, temperature and water salinity.

For the dynamic partitioning of the CO₂ stream, a special apparatus was designed and constructed which consists of a 0.952 cm ID Hastalloy high pressure tube 24.38 meters in length (labeled "Fat Tube" in the diagram). The tube is packed with 20/40 mesh silica rounded frac sand and coiled to allow placement in a heat bath to simulate reservoir temperature conditions. The sand has 37% porosity and permeability of 5915 mD. The silica sand was used to avoid possible geochemical reactions between the acidic brine saturated with dissolved H₂S and/or CO₂ and the mineral grains. A quartz strain gage pressure transducer is mounted across the coiled tube to allow differential pressure measurements. Fluids are stored in sour-gas rated piston cylinders and pulsation-free position-displacement injection pumps are used to displace the test fluid through the long packed tube at a fixed, known constant displacement rate. System pressure is controlled using a sour-gas service-rated backpressure regulator. Fluid samples are obtained in a three-phase separator where oil (no present in these tests), water and any gas phase volumes can be measured. The gas phase composition is determined by injection of the produced gas samples into a Hewlett Packard Series 5980 gas chromatograph with independent verification by titwtler titration (for H₂S concentrations). The titwtler method is a iodide based optical titration method that is commonly used on a field basis to verify H₂S contents in acid gases that involves no electronic instrumentation and hence provides a rapid verification of the accuracy of the gas chromatograph measurements.



Schematic representation of the apparatus used for measurements of differential arrival time of acid gas components under dynamic (flow) reservoir conditions.

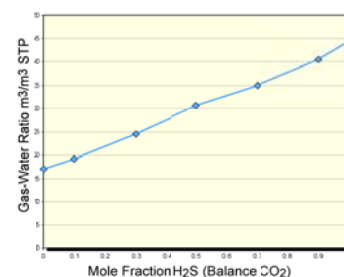


Pictures of the apparatus used for the dynamic measurements of arrival time of acid gas components. Outside view showing oven and displacement pump system (left) and inner illustration (right) showing long coiled sandpack in which experiments are conducted.



Experiments and Results

The static solubility tests were conducted by charging a specified volume of brine into the piston cell in the PVT apparatus and increasing temperature and pressure to the desired test conditions. Small amounts of the acid-gas mixture were then titrated into the cell under constant agitation until the first small bubble of free gas was observed, indicating that the saturation point of the brine had been reached at the specified operating conditions. Excess gas was then added to the system under agitation to simulate an 'equilibrium' brine situation approximating the zone of a reservoir where excess injected gas had contacted a given brine volume. The excess free gas was then removed at constant pressure and the remaining saturated brine was then flashed to ambient pressure and temperature. The gas-water solubility was measured and determination was made of the composition of the dissolved solution gas in the brine.

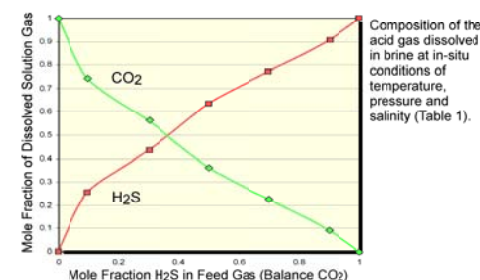


Solubility of acid gas in brine at in-situ conditions of temperature, pressure and water salinity (Table 1).

Table 1

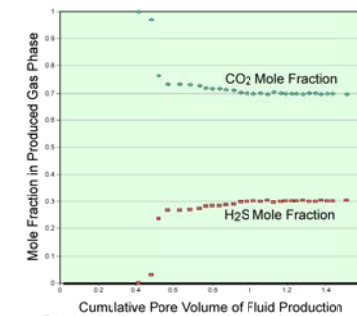
Pressure (kPa)	13,500
Temperature (°C)	61
Brine Salinity (ppm)	118,950
Porous Medium	200 mesh Silica Sand
Coil Tube Length (cm)	2438.4
Tube Diameter (cm)	0.775
Tube Cross-sectional Area (cm ²)	0.471
Porosity	0.37
Pore Volume (cm ³)	424.68
Permeability (mD)	5915
Displacement Rate (cm ³ /hr)	7.5

Characteristics of the static and dynamic partitioning experiments for conditions specific to the Sulphur Point aquifer at Zama in northwestern Alberta.

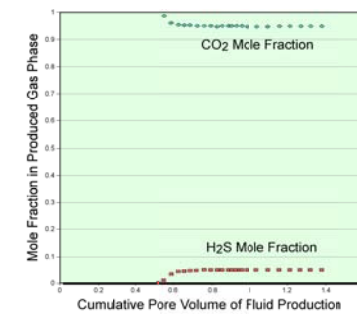


Composition of the acid gas dissolved in brine at in-situ conditions of temperature, pressure and salinity (Table 1).

The dynamic solubility tests for a stream of CO₂ containing 2%, 5% and 30% H₂S, show that gas with an initial composition of 100% CO₂ breaks through at the outlet of the coiled tube after approximately 0.45 pore volume (PV) of brine production, and that the concentration of the CO₂ progressively decreases while that of H₂S increases until the gas composition at outflow is the same as at the inflow after ~1 PV of produced fluids. The breakthrough of the contaminant gas depends on the gas, and for the same gas, on its concentration. For the same gas (e.g., H₂S), the breakthrough occurs faster if the impurity concentration is higher. The situation is reversed in the case of a CO₂ stream containing methane (CH₄). Methane has much lower solubility than CO₂ and shows first at the outflow (observation point).



Evolution of acid gas composition at the outlet of the experimental apparatus for an injected CO₂ stream containing 30% H₂S (left) and 2% H₂S (right). The gas mole fraction is presented on a logarithmic scale on the right figure.



Evolution of acid gas composition at the outlet of the experimental apparatus for an injected CO₂ stream containing 5% impurities: H₂S (left) and methane (CH₄) (right).

Conclusions

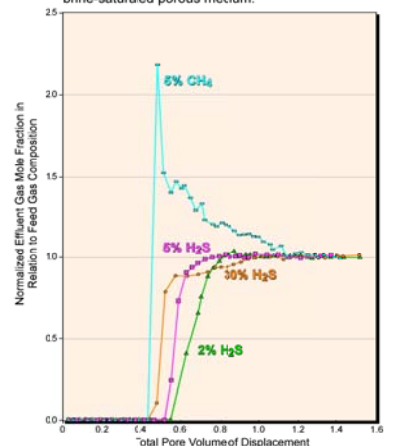
H₂S has higher solubility and lower k factor than CO₂ at standard and reservoir conditions, while CH₄ has lower solubility.

The high solubility of H₂S which results in a lower equilibrium ratio (mole fraction of H₂S in the gas phase vs. that dissolved in the liquid phase), in contrast to that of CO₂, results in suppressed H₂S concentrations at the leading edge of the breakthrough gas phase. This phenomenon suggests that selective dissolution effects will result in the leading edge of a plume of injected CO₂ containing H₂S in an aquifer being virtually pure CO₂. The relative speed of migration of the toxic H₂S phase through the water saturated reservoir rock is retarded, and, on a field basis, would provide advance warning of a potential future breakthrough of a toxic acid gas phase.

In the case of a CO₂ stream containing methane, the early show of methane will indicate that leakage of CO₂ from the storage site is occurring.

Experiments are ongoing for CO₂ and 5% SO₂, N₂, NO and NO₂

Compositional evolution of the effluent dissolved gas for an injected CO₂ stream containing various concentrations of H₂S and methane (CH₄) into a brine-saturated porous medium.



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